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ON FLUID CHLORINE;
AND
ON THE CONDENSATION OF SEVERAL GASES
INTO LIQUIDS.

BY
MR. MICHAEL FARADAY,
CHEMICAL ASSISTANT IN THE ROYAL INSTITUTION.

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W. T. BRANDE, Sec. R. S.

ON FLUID CHLORINE, &c.

Read before the ROYAL SOCIETY, March 13, 1823.

IT is well known that before the year 1810, the solid substance obtained by exposing chlorine, as usually procured, to a low temperature, was considered as the gas itself reduced into that form; and that SIR HUMPHRY DAVY first showed it to be a hydrate, the pure dry gas not being condensible even at a temperature of -40° F.

I took advantage of the late cold weather to procure crystals of this substance for the purpose of analysis. The results are contained in a short paper in the Quarterly Journal of Science, Vol. XV. Its composition is very nearly 27.7 chlorine, 72.3 water, or 1 proportional of chlorine, and 10 of water.

The President of the Royal Society having honoured me by looking at these conclusions, suggested, that an exposure of the substance to heat under pressure, would probably lead to interesting results; the following experiments were commenced at his request. Some hydrate of chlorine was prepared, and being dried as well as could be by pressure in bibulous paper, was introduced into a sealed glass tube, the upper end of which was then hermetically closed. Being placed in water at 60° , it underwent no change; but when put into water at 100° , the substance fused, the tube became

filled with a bright yellow atmosphere, and, on examination, was found to contain two fluid substances: the one, about three-fourths of the whole, was of a faint yellow colour, having very much the appearance of water; the remaining fourth was a heavy bright yellow fluid, lying at the bottom of the former, without any apparent tendency to mix with it. As the tube cooled, the yellow atmosphere condensed into more of the yellow fluid, which floated in a film on the pale fluid, looking very like chloride of nitrogen; and at 70° the pale portion congealed, although even at 32° the yellow portion did not solidify. Heated up to 100° the yellow fluid appeared to boil, and again produced the bright coloured atmosphere.

By putting the hydrate into a bent tube, afterwards hermetically sealed, I found it easy, after decomposing it by a heat of 100° , to distil the yellow fluid to one end of the tube, and so separate it from the remaining portion. In this way a more complete decomposition of the hydrate was effected, and, when the whole was allowed to cool, neither of the fluids solidified at temperatures above 34° , and the yellow portion not even at 0° . When the two were mixed together they gradually combined at temperatures below 60° , and formed the same solid substances as that first introduced. If, when the fluids were separated, the tube was cut in the middle, the parts flew asunder as if with an explosion, the whole of the yellow portion disappeared, and there was a powerful atmosphere of chlorine produced; the pale portion on the contrary remained, and when examined, proved to be a weak solution of chlorine in water, with a little muriatic acid, probably from the impurity of the hydrate used. When that end of the tube in which the yellow fluid lay was broken under

a jar of water, there was an immediate production of chlorine gas.

I at first thought that muriatic acid and euchlorine had been formed; then, that two new hydrates of chlorine had been produced; but at last I suspected that the chlorine had been entirely separated from the water by the heat, and condensed into a dry fluid by the mere pressure of its own abundant vapour. If that were true, it followed, that chlorine gas, when compressed, should be condensed into the same fluid, and, as the atmosphere in the tube in which the fluid lay was not very yellow at 50° or 60° , it seemed probable that the pressure required was not beyond what could readily be obtained by a condensing syringe. A long tube was therefore furnished with a cap and stop-cock, then exhausted of air and filled with chlorine, and being held vertically with the syringe upwards, air was forced in, which thrust the chlorine to the bottom of the tube, and gave a pressure of about 4 atmospheres. Being now cooled, there was an immediate deposit in films, which appeared to be hydrate, formed by water contained in the gas and vessels, but some of the yellow fluid was also produced. As this however might also contain a portion of the water present, a perfectly dry tube and apparatus were taken, and the chlorine left for some time over a bath of sulphuric acid before it was introduced. Upon throwing in air and giving pressure, there was now no solid film formed, but the clear yellow fluid was deposited, and more abundantly still upon cooling. After remaining some time it disappeared, having gradually mixed with the atmosphere above it, but every repetition of the experiment produced the same results.

Presuming that I had now a right to consider the yellow fluid as pure chlorine in the liquid state, I proceeded to examine its properties, as well as I could when obtained by heat from the hydrate. However obtained, it always appears very limpid and fluid, and excessively volatile at common pressure. A portion was cooled in its tube to 0° : it remained fluid. The tube was then opened, when a part immediately flew off, leaving the rest so cooled by the evaporation as to remain a fluid under the atmospheric pressure. The temperature could not have been higher than -40° in this case; as Sir HUMPHRY DAVY has shown that dry chlorine does not condense at that temperature under common pressure. Another tube was opened at a temperature of 50° ; a part of the chlorine volatilised, and cooled the tube so much as to condense the atmospheric vapour on it as ice.

A tube having the water at one end and the chlorine at the other was weighed, and then cut in two; the chlorine immediately flew off, and the loss being ascertained was found to be 1.6 grains: the water left was examined and found to contain some chlorine: its weight was ascertained to be 5.4 grains. These proportions, however, must not be considered as indicative of the true composition of hydrate of chlorine; for, from the mildness of the weather during the time when these experiments were made, it was impossible to collect the crystals of hydrate, press, and transfer them, without losing much chlorine; and it is also impossible to separate the chlorine and water in the tube perfectly, or keep them separate, as the atmosphere within will combine with the water, and gradually reform the hydrate.

Before cutting the tube, another tube had been prepared

exactly like it in form and size, and a portion of water introduced into it, as near as the eye could judge, of the same bulk as the fluid chlorine: this water was found to weigh 1.2 grains; a result, which, if it may be trusted, would give the specific gravity of fluid chlorine as 1.33; and from its appearance in, and on water, this cannot be far wrong.

Note on the condensation of Muriatic Acid Gas into the liquid form. By Sir H. DAVY, Bart. Pres. R. S.

IN desiring Mr. FARADAY to expose the hydrate of chlorine to heat in a closed glass tube, it occurred to me, that one of three things would happen; that it would become fluid as a hydrate; or that a decomposition of water would occur, and euchlorine and muriatic acid be formed; or that the chlorine would separate in a condensed state. This last result having been obtained, it evidently led to other researches of the same kind. I shall hope, on a future occasion, to detail some general views on the subject of these researches. I shall now merely mention, that by sealing muriate of ammonia and sulphuric acid in a strong glass tube, and causing them to act upon each other, I have procured liquid muriatic acid: and by substituting carbonate for muriate of ammonia, I have no doubt that carbonic acid may be obtained, though in the only trial I have made the tube burst. I have requested Mr. FARADAY to pursue these experiments, and to extend them to all the gases which are of considerable density, or to any extent soluble in water; and I hope soon to be able to lay an account of his results, with

some applications of them that I propose to make, before the Society.

I cannot conclude this note without observing, that the generation of elastic substances in close vessels, either with or without heat, offers much more powerful means of approximating their molecules than those dependent upon the application of cold, whether natural or artificial: for, as gases diminish only about $\frac{1}{480}$ in volume for every — degree of FAHRENHEIT's scale, beginning at ordinary temperatures, a very slight condensation only can be produced by the most powerful freezing mixtures, not half as much as would result from the application of a strong flame to one part of a glass tube, the other part being of ordinary temperature: and when attempts are made to condense gases into fluids by sudden mechanical compression, the heat, instantly generated, presents a formidable obstacle to the success of the experiment; whereas, in the compression resulting from their slow generation in close vessels, if the process be conducted with common precautions, there is no source of difficulty or danger; and it may be easily assisted by artificial cold in cases when gases approach near to that point of compression and temperature at which they become vapours.

ON THE CONDENSATION OF SEVERAL GASES INTO LIQUIDS.

Read before the ROYAL SOCIETY, April 10, 1823.

I HAD the honour, a few weeks since, of submitting to the Royal Society a paper on the reduction of chlorine to the liquid state. An important note was added to the paper by the President, on the general application of the means used in this case to the reduction of other gaseous bodies to the liquid state ; and in illustration of the process, the production of liquid muriatic acid was described. Sir HUMPHRY DAVY did me the honour to request I would continue the experiments, which I have done under his general direction, and the following are some of the results already obtained :

Sulphurous Acid.

Mercury and concentrated sulphuric acid were sealed up in a bent tube, and, being brought to one end, heat was carefully applied, whilst the other end was preserved cool by wet bibulous paper. Sulphurous acid gas was produced where the heat acted, and was condensed by the sulphuric acid above ; but, when the latter had become saturated, the sulphurous acid passed to the cold end of the tube, and was condensed into a liquid. When the whole tube was cold, if the sulphurous acid were returned on to the mixture of

sulphuric acid and sulphate of mercury, a portion was re-absorbed, but the rest remained on it without mixing.

Liquid sulphurous acid is very limpid and colourless, and highly fluid. Its refractive power, obtained by comparing it in water and other media, with water contained in a similar tube, appeared to be nearly equal to that of water. It does not solidify or become adhesive at a temperature of 0° F. When a tube containing it was opened, the contents did not rush out as with explosion, but a portion of the liquid evaporated rapidly, cooling another portion so much as to leave it in the fluid state at common barometric pressure. It was however rapidly dissipated, not producing visible fumes, but producing the odour of pure sulphurous acid, and leaving the tube quite dry. A portion of the vapour of the fluid received over a mercurial bath, and examined, proved to be sulphurous acid gas. A piece of ice dropped into the fluid instantly made it boil, from the heat communicated by it.

To prove in an unexceptionable manner that the fluid was pure sulphurous acid, some sulphurous acid gas was carefully prepared over mercury, and a long tube perfectly dry, and closed at one end, being exhausted, was filled with it; more sulphurous acid was then thrown in by a condensing syringe, till there were three or four atmospheres; the tube remained perfectly clear and dry, but on cooling one end to 0° , the fluid sulphurous acid condensed, and in all its characters was like that prepared by the former process.

A small gage was attached to a tube in which sulphurous acid was afterwards formed, and at a temperature of 45° F. the pressure within the tube was equal to three atmospheres, there being a portion of liquid sulphurous acid present: but

as the common air had not been excluded when the tube was sealed, nearly one atmosphere must be due to its presence, so that sulphurous acid vapour exerts a pressure of about two atmospheres at 45° F. Its specific gravity was nearly 1.42.*

Sulphuretted hydrogen.

A tube being bent, and sealed at the shorter end, strong muriatic acid was poured in through a small funnel, so as nearly to fill the short leg without soiling the long one. A piece of platinum foil was then crumpled up and pushed in, and upon that were put fragments of sulphuret of iron, until the tube was nearly full. In this way action was prevented until the tube was sealed. If it once commences, it is almost impossible to close the tube in a manner sufficiently strong, because of the pressing out of the gas. When closed, the muriatic acid was made to run on to the sulphuret of iron, and then left for a day or two. At the end of that time, much proto-muriate of iron had formed, and on placing the

* I am indebted to Mr. DAVIES GILBERT, who examined with much attention the results of these experiments, for the suggestion of the means adopted to obtain the specific gravity of some of these fluids. A number of small glass bulbs were blown and hermetically sealed; they were then thrown into alcohol, water, sulphuric acid, or mixtures of these, and when any one was found of the same specific gravity as the fluid in which it was immersed, the specific gravity of the fluid was taken: thus a number of hydrometrical bulbs were obtained; these were introduced into the tubes in which the substances were to be liberated; and ultimately, the dry liquids obtained, in contact with them. It was then observed whether they floated or not, and a second set of experiments were made with bulbs lighter or heavier as required, until a near approximation was obtained. Many of the tubes burst in the experiments, and in others difficulties occurred from the accidental fouling of the bulb by the contents of the tube. One source of error may be mentioned in addition to those which are obvious, namely, the alteration of the bulk of the bulb by its submission to the pressure required to keep the substance in the fluid state.

clean end of the tube in a mixture of ice and salt, warming the other end if necessary by a little water, sulphuretted hydrogen in the liquid state distilled over.

The liquid sulphuretted hydrogen was colourless, limpid, and excessively fluid. Ether, when compared with it in similar tubes, appeared tenacious and oily. It did not mix with the rest of the fluid in the tube, which was no doubt saturated, but remained standing on it. When a tube containing it was opened, the liquid immediately rushed into vapour; and this being done under water, and the vapour collected and examined, it proved to be sulphuretted hydrogen gas. As the temperature of a tube containing some of it rose from 0° to 45° , part of the fluid rose in vapour, and its bulk diminished; but there was no other change: it did not seem more adhesive at 0° than at 45° . Its refractive power appeared to be rather greater than that of water; it decidedly surpassed that of sulphurous acid. A small gage being introduced into a tube in which liquid sulphuretted hydrogen was afterwards produced, it was found that the pressure of its vapour was nearly equal to 17 atmospheres at the temperature of 50° .

The gages used were made by drawing out some tubes at the blow-pipe table until they were capillary, and of a trumpet form; they were graduated by bringing a small portion of mercury successively into their different parts; they were then sealed at the fine end, and a portion of mercury placed in the broad end; and in this state they were placed in the tubes, so that none of the substances used, or produced, could get to the mercury, or pass by it to the inside of the gage. In estimating the number of atmospheres, one has always been subtracted for the air left in the tube.

The specific gravity of sulphuretted hydrogen appeared to be 0.9.

Carbonic acid.

The materials used in the production of carbonic acid, were carbonate of ammonia and concentrated sulphuric acid; the manipulation was like that described for sulphuretted hydrogen. Much stronger tubes are however required for carbonic acid than for any of the former substances, and there is none which has produced so many or more powerful explosions. Tubes which have held fluid carbonic acid well for two or three weeks together, have, upon some increase in the warmth of the weather, spontaneously exploded with great violence; and the precautions of glass masks, goggles, &c. which are at all times necessary in pursuing these experiments, are particularly so with carbonic acid.

Carbonic acid is a limpid colourless body, extremely fluid, and floating upon the other contents of the tube. It distils readily and rapidly at the difference of temperature between 32° and 0° . Its refractive power is much less than that of water. No diminution of temperature to which I have been able to submit it, has altered its appearance. In endeavouring to open the tubes at one end, they have uniformly burst into fragments, with powerful explosions. By inclosing a gage in a tube in which fluid carbonic acid was afterwards produced, it was found that its vapour exerted a pressure of 36 atmospheres at a temperature of 32° .

It may be questioned, perhaps, whether this and other similar fluids obtained from materials containing water, do not contain a portion of that fluid; in as much as its absence has not been proved, as it may be with chlorine, sulphurous

acid, cyanogen, and ammonia. But besides the analogy which exists between the latter and the former, it may also be observed in favour of their dryness, that any diminution of temperature causes the deposition of a fluid from the atmosphere, precisely like that previously obtained; and there is no reason for supposing that these various atmospheres, remaining as they do in contact with concentrated sulphuric acid, are not as dry as atmospheres of the same kind would be over sulphuric acid at common pressure.

Euchlorine.

Fluid euchlorine was obtained by inclosing chlorate of potash and sulphuric acid in a tube, and leaving them to act on each other for 24 hours. In that time there had been much action, the mixture was of a dark reddish brown, and the atmosphere of a bright yellow colour. The mixture was then heated up to 100° , and the unoccupied end of the tube cooled to 0° ; by degrees the mixture lost its dark colour, and a very fluid ethereal looking substance condensed. It was not miscible with a small portion of the sulphuric acid which lay beneath it; but when returned on to the mass of salt and acid, it was gradually absorbed, rendering the mixture of a much deeper colour even than itself.

Euchlorine thus obtained is a very fluid transparent substance, of a deep yellow colour. A tube containing a portion of it in the clean end, was opened at the opposite extremity; there was a rush of euchlorine vapour, but the salt plugged up the aperture: whilst clearing this away, the whole tube burst with a violent explosion, except the small end in a cloth in my hand, where the euchlorine previously lay, but the fluid had all disappeared.

Nitrous oxide.

Some nitrate of ammonia, previously made as dry as could be by partial decomposition, by heat in the air, was sealed up in a bent tube, and then heated in one end, the other being preserved cool. By repeating the distillation once or twice in this way, it was found, on after-examination, that very little of the salt remained undecomposed. The process requires care. I have had many explosions occur with very strong tubes, and at considerable risk.

When the tube is cooled, it is found to contain two fluids, and a very compressed atmosphere. The heavier fluid on examination proved to be water, with a little acid and nitrous oxide in solution; the other was nitrous oxide. It appears in a very liquid, limpid, colourless state; and so volatile that the warmth of the hand generally makes it disappear in vapour. The application of ice and salt condenses abundance of it into the liquid state again. It boils readily by the difference of temperature between 50° and 0° . It does not appear to have any tendency to solidify at -10° . Its refractive power is very much less than that of water, and less than any fluid that has yet been obtained in these experiments, or than any known fluid. A tube being opened in the air, the nitrous oxide immediately burst into vapour. Another tube opened under water, and the vapour collected and examined, it proved to be nitrous oxide gas. A gage being introduced into a tube, in which liquid nitrous oxide was afterwards produced, gave the pressure of its vapour as equal to above 50 atmospheres at 45° .

Cyanogen.

Some pure cyanuret of mercury was heated until perfectly dry. A portion was then inclosed in a green glass tube, in the same manner as in former instances, and being collected to one end, was decomposed by heat, whilst the other end was cooled. The cyanogen soon appeared as a liquid: it was limpid, colourless, and very fluid; not altering its state at the temperature of 0° . Its refractive power is rather less, perhaps, than that of water. A tube containing it being opened in the air, the expansion within did not appear to be very great; and the liquid passed with comparative slowness into the state of vapour, producing great cold. The vapour, being collected over mercury, proved to be pure cyanogen.

A tube was sealed up with cyanuret of mercury at one end, and a drop of water at the other; the fluid cyanogen was then produced in contact with the water. It did not mix, at least in any considerable quantity, with that fluid, but floated on it, being lighter, though apparently not so much so as ether would be. In the course of some days, action had taken place, the water had become black, and changes, probably such as are known to take place in an aqueous solution of cyanogen, occurred. The pressure of the vapour of cyanogen appeared by the gage to be 3.6 or 3.7 atmospheres at 45° F. Its specific gravity was nearly 0.9.

Ammonia.

In searching after liquid ammonia, it became necessary, though difficult, to find some dry source of that substance; and I at last resorted to a compound of it, which I had occa-

sion to notice some years since with chloride of silver.* When dry chloride of silver is put into ammoniacal gas, as dry as it can be made, it absorbs a large quantity of it; 100 grains condensing above 130 cubical inches of the gas: but the compound thus formed is decomposed by a temperature of 100° F. or upwards. A portion of this compound was sealed up in a bent tube and heated in one leg, whilst the other was cooled by ice or water. The compound thus heated under pressure fused at a comparatively low temperature, and boiled up, giving off ammoniacal gas, which condensed at the opposite end into a liquid.

Liquid ammonia thus obtained was colourless, transparent, and very fluid. Its refractive power surpassed that of any other of the fluids described, and that also of water itself. From the way in which it was obtained, it was evidently as free from water as ammonia in any state could be. When the chloride of silver is allowed to cool, the ammonia immediately returns to it, combining with it, and producing the original compound. During this action a curious combination of effects takes place: as the chloride absorbs the ammonia, heat is produced, the temperature rising up nearly to 100°; whilst a few inches off, at the opposite end of the tube, considerable cold is produced by the evaporation of the fluid. When the whole is retained at the temperature of 60°, the ammonia boils till it is dissipated and re-combined. The pressure of the vapour of ammonia is equal to about 6.5 atmospheres at 50°. Its specific gravity was 0.76.

* Quarterly Journal of Science, vol. V. p. 74.

Muriatic acid,

When made from pure muriate of ammonia and sulphuric acid, liquid muriatic acid is obtained colourless, as Sir HUMPHRY DAVY had anticipated. Its refractive power is greater than that of nitrous oxide, but less than that of water; it is nearly equal to that of carbonic acid. The pressure of its vapour at the temperature of 50° , is equal to about 40 atmospheres.

Chlorine.

The refractive power of fluid chlorine is rather less than that of water. The pressure of its vapour at 60° is nearly equal to 4 atmospheres.

Attempts have been made to obtain hydrogen, oxygen, fluoboric, fluosilicic, and phosphuretted hydrogen gases in the liquid state; but though all of them have been subjected to great pressure, they have as yet resisted condensation. The difficulty with regard to fluoboric gas consists, probably, in its affinity for sulphuric acid, which, as Dr. DAVY has shown, is so great as to raise the sulphuric acid with it in vapour. The experiments will however be continued on these and other gases, in the hopes that some of them, at least, will ultimately condense.